



PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Organosilicon Compounds and process for producing same

We, UNION CARBIDE CORPORATION, of 270 Park Avenue, New York, State of New York, United States of America, a Corporation organised under the laws of the State of New York, United States of America (Assignee of RONALD MARSTON PIKE jointly with EDWARD LEWIS MOREHOUSE), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates in general to the synthesis of novel organosilicon compounds. More particularly, the invention is concerned with processes for the production of organosilicon compounds, containing among other possible functional groups, a substituted

amino group linked to the silicon atom or atoms thereof through a polymethylene linkage of at least three carbon atoms.

The present invention is based, in part, upon our discovery that organosilicon compounds containing a substituted amino group attached to the silicon atom thereof through a polymethylene linkage of at least three carbon atoms can be produced by reacting an amino silicon compound containing the grouping $\text{H}_2\text{N}(\text{CH}_2)_a\text{Si}\equiv$, wherein a is an integer of at least 3, with alpha-beta olefinically unsaturated organic compounds. The overall reaction can be graphically represented by the following equation which depicts for the purpose of illustration, the reaction between an aminoalkyl silicon compound and acrylonitrile:



Our process can be carried out by forming a mixture of the aminoalkyl silicon compound and an alpha-beta olefinically unsaturated organic compound under conditions which cause the starting materials to react. There results an organosilicon compound containing an organo-substituted amino group bonded to the silicon atom thereof through a polymethylene linkage of at least three carbon atoms by the addition of the grouping $-\text{NH}(\text{CH}_2)_a\text{Si}\equiv$ to the beta-olefinic carbon atom of the starting unsaturated organic compound and by the addition of hydrogen to the alpha-olefinic carbon atom thereof.

According to our studies the basic reaction is equally applicable to all organosilicon compounds containing the aminoalkylsilyl grouping depicted above. Most suitable for use in our process are the aminoalkyl alkoxysilanes and the aminoalkyl polysiloxanes, including copolymeric materials which contain both aminoalkylsiloxane and hydrocarbon siloxane units. Typical of the aminoalkylalkoxysilanes which we can employ as our organosilicon starting

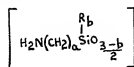
materials are those compounds represented by the structural formula:



herein R represents an alkyl group such as methyl, ethyl, propyl and butyl, or an aryl group such as phenyl, naphthyl and tolyl, Y represents an alkoxy group such as methoxy, ethoxy and propoxy, a is an integer of at least 3, preferably 3 or 4 and b is 0, 1 or 2, preferably 0 or 1. Illustrative of such aminoalkylalkoxysilanes are gamma - aminopropyltriethoxysilane, gamma - aminopropyltripropoxysilane, gamma - aminopropylethoxydiethoxysilane, gamma - aminopropylphenyldiethoxysilane, delta - aminobutyltriethoxysilane, delta - aminobutylmethoxydiethoxysilane, delta - aminobutylethoxydiethoxysilane and delta - aminobutylphenyldiethoxysilane.

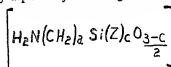
Typical of the aminoalkylpolysiloxanes suitable for use as our organosilicon starting

materials are those of polysiloxanes which contain the structural unit:



wherein R_b , a and b have the same values described above. Such polysiloxanes are prepared by the hydrolysis and condensation of those aminoalkylalkoxysilanes described above or by the co-hydrolysis and co-condensation of such aminoalkylalkoxysilanes with other hydrolyzable silanes and can include: aminoalkylpolysiloxanes of the trifunctional variety (i.e. where $b=0$), aminoalkylalkyl- and aminoalkylarylalkylsiloxanes of the difunctional variety which include the cyclic or linear polysiloxanes (i.e. where $b=1$) and linear aminoalkylalkyl- aminoalkylidyl- and aminoalkylarylalkylidylsiloxanes of the monofunctional variety (i.e. where $b=2$) as well as mixtures of compounds produced by the co-hydrolysis of difunctional, trifunctional and mono-functional aminoalkylsilanes.

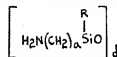
Suitable starting aminoalkylpolysiloxanes of the trifunctional variety can be more specifically depicted by the average formula:



wherein a has the value previously described, Z represents an hydroxyl and/or alkoxy group and c has an average value of from 0 to 2, but is preferably from 0.1 to 1. Aminoalkylpolysiloxanes of this variety which are essentially free of silicon-bonded alkoxy or hydroxyl groups (i.e. where $c=0$) can be prepared by the complete hydrolysis and complete condensation of aminoalkyltrialkoxysilanes, whereas aminoalkylpolysiloxanes in which Z is predominantly alkoxy, can be prepared by the partial hydrolysis and complete condensation of the same starting silanes. One the other hand, aminoalkylpolysiloxanes in which Z is predominately hydroxyl, can be prepared by the essentially complete hydrolysis and partial condensation of the same aminoalkyltrialkoxysilanes. By way of illustration, a gamma-aminopropylpolysiloxane containing silicon-bonded ethoxy groups can be prepared by hydrolyzing gamma-aminopropyltriethoxysilane with an amount of water insufficient to react with all of the silicon-bonded ethoxy groups present in the starting silane and subsequently condensing the hydrolyzate so produced to obtain the desired polymer.

Suitable starting aminoalkylpolysiloxanes of

the difunctional variety which include the cyclic and linear polysiloxanes can be more specifically defined by the structural formula:

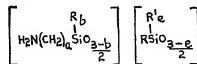


wherein R and a have the values previously described and d is an integer of at least 3 and can be as high as 7 for the cyclic aminoalkylpolysiloxanes and higher for the linear aminoalkylpolysiloxanes. Such cyclic and linear aminoalkylpolysiloxanes can be prepared by the hydrolysis and condensation of aminoalkylalkyl- or aminoalkylarylalkylsiloxanes. In carrying out the hydrolysis and condensation procedures there is produced a product comprising a mixture of cyclic and linear polysiloxanes from which the desired polysiloxane can be recovered. Illustrative of the cyclic aminoalkylsiloxanes suitable for use as the organo-silicon starting material in our process are the cyclic tetramer of gamma-aminopropylmethoxysilane and the cyclic tetramer of delta-aminobutylphenylsiloxane. Illustrative of suitable linear aminoalkylpolysiloxanes are gamma-aminopropylmethylpolysiloxane, gamma-aminopropylethylpolysiloxane and delta-aminobutylmethylpolysiloxane.

Included among the useful starting linear aminoalkylpolysiloxanes are the alkyl, alkoxy and hydroxyl terminated polysiloxanes which contain from 1 to 3 of such groups bonded to the terminal silicon atoms of the molecules comprising the polymeric chains. Thus we can also employ as our starting materials such linear aminoalkylpolysiloxanes as mono-ethoxy terminated gamma-aminopropylethylpolysiloxane or methyldiethoxysilyl terminated delta-aminobutylmethylpolysiloxane or mono-ethoxydimethylsilyl terminated gamma-aminopropylphenylpolysiloxane. The linear aminoalkylalkyl- and aminoalkylarylpolysiloxanes useful in our process can be prepared by the equilibration of cyclic aminoalkylsiloxanes with silicon compounds containing predominately silicon-bonded alkoxy groups, or by the co-hydrolysis and condensation of trialkylalkoxysilanes with aminoalkylalkyl- or aminoalkylarylalkylidethoxysilanes.

Hydroxy end-blocked linear polysiloxanes can be prepared by heating linear or cyclic aminoalkylpolysiloxanes with water.

The copolymeric aminoalkylpolysiloxanes which can be employed as a starting material can be depicted as containing both the structural units:



wherein R, α and b have the values described above, R¹ represents either an alkyl or aryl group as R₂ and e is 0, 1 or 2. The copolymers suitable for use as the organosilicon starting material in our process can contain various combined siloxane units such as trifunctional aminoalkylsiloxane units (where $b=0$) with trifunctional alkyl, aryl, or mixed, alkyl- and aryl-siloxane units (where $e=0$) or with difunctional alkyl-, aryl- or mixed alkyl- and arylsiloxane units (where $e=1$). These copolymers can also contain various combined siloxane units; difunctional aminoalkylsiloxane units (where $b=1$) with trifunctional alkyl-, aryl- or mixed alkyl- and aryl-siloxane units (where $e=0$) or with difunctional alkyl-, aryl- or mixed alkyl- and arylsiloxane units (where $e=1$).

These copolymers which contain trifunctional aminoalkylsiloxane units and other siloxane units are preferably prepared by the co-hydrolysis and co-condensation of the corresponding alkoxysilane starting materials. Such copolymers can contain silicon-bonded alkoxy or hydroxyl groups or they can comprise essentially completely condensed materials. The linear and cyclic copolymeric siloxanes are preferably prepared by the separate hydrolysis and condensation of an aminoalkylalkyldialkoxysilane or aminoalkylaryldialkoxysilane and the dialkyldialkoxysilane or diaryldialkoxysilane to cyclic aminoalkylsiloxanes and cyclic dialkylsiloxanes or diarylsiloxanes and subsequently equilibrating mixtures of such cyclic siloxanes to linear copolymers. Such linear copolymers can also contain chain-terminating or end-blocking groups such as alkyl, alkoxy or hydroxyl groups.

The aminoalkylalkoxysilanes and aminoalkylpolyolsiloxanes as well as copolymers containing aminoalkylsiloxane and hydrocarbylsiloxane units are all described in copending applications Nos. 30925/57, 30936/57, 30945/57 and 20473/61 (Serial Nos. 882,053, 882,056, 882,052 and 882,059). Processes for producing such compounds are also described in said copending applications.

The alpha-beta olefinically unsaturated organic compounds which we can employ as one of the starting materials in our process are those compounds which contain an organic functional group bonded to at least one of the olefinic carbon atoms thereof. Such compounds can be graphically depicted by the following formula:



wherein R^{II} represents either a hydrogen atom or an alkyl group, X represents a nitrile group or a substituted carbonyl group represented by the structure:



wherein D represents, hydrogen, or an alkyl, aryl, alkoxy, aryloxy or an amino group, and B represents a hydrogen atom, an alkyl group, an aryl group or the radical X. Illustrative of the alpha-beta olefinically unsaturated organic compounds suitable for use in our process are: acrylonitrile, crotononitrile, methyl acrylate, ethyl acrylate, methyl methacrylate, acrylamide, ethyl cinnamate, diethyl maleate and methyl vinylketone and the like.

The olefinically unsaturated compound and the aminoalkyl silicon compound starting materials can be employed in amounts of from 1 to 3 chemical equivalents of the unsaturated compound (based on the olefine group) per chemical equivalent of the aminoalkyl silicon compound (based on the amino group). Preferably, we employ our starting materials in equal chemically equivalent amounts. However, amounts of our starting materials, other than that set forth above, can also be employed, although no commensurate advantage is obtained.

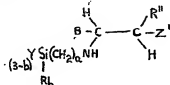
The reaction between an alpha-beta olefinically unsaturated organic compound and an aminoalkyl silicon compound is mildly exothermic and can be carried out at temperatures as low as 10° C. and at temperatures up to 150° C. and higher. In carrying out our process, we prefer to conduct the reaction at temperatures of from about 30° C. to about 80° C. The reaction can be carried out at temperatures outside of the range described above, however no apparent advantage is gained thereby.

Our process can be carried out by conducting the reaction between the starting materials within a liquid organic compound which is miscible therewith, but with which it is non-reactive. Suitable for use as solvents are: the aromatic hydrocarbons, such as benzene and toluene, and the dialkyl ethers, such as diethyl ether and diisopropyl ether. The amount of the liquid organic compounds which can be employed in our process is not narrowly critical and can vary over a wide range. We can employ from about 50 parts to about 200 parts of such compounds per 100 parts of the starting materials.

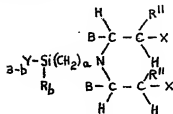
In the practice of the process of our invention we prefer to employ as our starting alpha-beta olefinically unsaturated organic materials those compounds which contain only one organic functional group bonded to either of the olefinic carbon atoms thereof. Furthermore, when the organic functional group bonded to an olefinic carbon atom of our starting materials is an aldehyde or ketone group we have found that a competing reaction occurs, namely that between such group and the amino group of our starting silicon

compounds to yield a methylenaminalkyl silicon compound. This reaction is the basis of the process and resulting products of our copending application No. 30939/57. In the process of the present invention this side reaction is undesirable and can be limited by first inactivating the aldehyde or ketone group toward such reactions, by known procedures, conducting our reaction and subsequently recovering the aldehyde or ketone group, again by known procedures.

The monomeric compounds of our invention are substituted aminoalkylalkoxysilanes and can be graphically depicted by the formula:

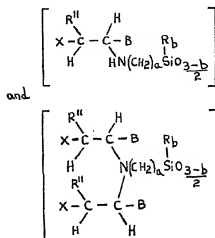


wherein Z^1 is an aminoalkyl radical or the radical represented by X and wherein R , R^1 , X, B, Y, a and b have the values defined above. The monomeric compounds of our invention can also include the bis-substituted aminoalkylalkoxysilanes which have the graphic formula:



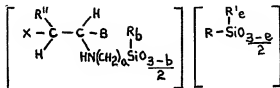
again wherein R , R^1 , X, B, Y, a and b have the values defined above. Illustrative of such substituted aminoalkylalkoxysilanes are gamma - (N - 2 - carbomethoxyethyl)aminopropyltriethoxysilane; gamma - (N,N - di - 2 - carbomethoxyethyl)aminopropyltriethoxysilane; delta - (N - 2 - carbomethoxyethyl)aminobutyltriethoxysilane; gamma - (N - 2 - amidoethyl)aminopropyltriethoxysilane; delta - (N - 2 - cyanoethyl)aminobutylmethyldiethoxysilane and delta - (N - 1 - phenyl - 2 - carbomethoxyethyl)aminobutylmethyldiethoxysilane.

The polymeric compounds of our invention, which can be prepared by the hydrolysis of the substituted aminoalkylalkoxysilanes described above or by the reaction of alpha-beta olefinically unsaturated organic compounds with aminoalkylpolysiloxanes have the structural units:



wherein R , R^1 , X, B, a and b have the values defined above. Illustrative of such polysiloxanes are: gamma - (N - 2 - carbomethoxyethyl)aminopropylpolysiloxane; gamma - (N,N - di - 2 - carbomethoxyethyl)aminopropylpolysiloxane; delta - (N - 2 - amidoethyl)aminobutylpolysiloxane; delta - (N - 2 - cyanoethyl)aminobutylpolysiloxane; the linear gamma - (N - 2 - carbomethoxyethyl)aminopropylmethylpolysiloxane, as well as the linear polymers thereof, the cyclic and linear delta - (N - 1 - phenyl - 2 - carbomethoxyethyl)aminobutylphenylsiloxanes and the linear and cyclic gamma - (N - 2 - amidoethyl) - aminopropylethylsiloxanes, as well as the corresponding disiloxanes.

The copolymeric compounds of our invention contain either of the polymeric units depicted immediately above and hydrocarbylpolysiloxane units. To illustrate, the mono-substituted aminoalkyl copolymeric siloxanes are represented by the units:



wherein R, R', R¹¹, X, B, (a) (b) and (c) have the values defined above. Such copolymers include among others the gamma-(N - 2 - carbomethoxyethyl)aminopropylmethyloxysilane; the delta-(N - 2 - amidoethyl)aminobutylethylsiloxane; and the delta-(N - 2 - cyanoethyl)aminobutylphenylsiloxane-modified dimethylpolysiloxane oils.

The cyanoalkyl substituted aminoalkylalkoxysilanes and cyanoalkyl substituted aminoalkylpolysiloxanes of our invention find use as the starting materials in preparing aminoalkyl substituted aminoalkylalkoxysilanes and aminoalkyl substituted aminoalkylpolysiloxanes. Such is accomplished by reacting the cyanoalkyl substituted aminoalkyl silicon compounds with hydrogen, under a pressure of at least 500 psi. The reaction can be conducted in the presence of ammonia and at a temperature of at least 50° C. and preferably at a temperature of from about 80° C. to about 120° C.

The compounds of our invention, including the aminoalkyl substituted aminoalkyl silicon compounds, find use as sizes for fibrous materials, particularly fibrous glass materials employed in combination with thermosetting resins. The difunctional polysiloxanes find use as modifiers for dimethylpolysiloxane oils and gums while the mono-functional disiloxanes find use as chain end-blocking units for dimethylpolysiloxane oils. The trifunctional polysiloxanes find use themselves as thermosetting resins or they can be employed to modify the known methyl- and methylphenyl thermosetting resins, both types of which are employed as coatings resistant to degradation at elevated temperatures. Our

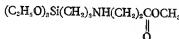
monomeric and polymeric compounds can also be employed as adhesives or as flocculation agents.

The following examples are illustrative of our invention:

EXAMPLE I

Reaction of Gamma-Aminopropyltriethoxysilane with Methyl Acrylate

To a 500 cc. flask equipped with a stirrer, thermometer and reflux condenser was charged 75.0 grams of gamma-aminopropyltriethoxysilane and 29.2 grams of methyl acrylate. The reaction mixture was heated to a temperature of 80° C., with constant stirring, under a pressure of 2.0 mm. of mercury; the resulting product (82.9 grams) had a refractive index at 25° C. of 1.4311 and a viscosity of 10 centipoises. The product was placed in a 250 cc. flask and distilled through a fractionating column under reduced pressure until 7.1 grams of a first fraction, with a boiling range from 55° C. (at 0.55 mm. of Hg) to 104° C. (at 0.38 mm. Hg) and having refractive indices at 25° C. of 1.4187-1.4208 was collected. At a pressure of 0.33-0.38 mm. of Hg and a temperature of 109° C.-111° C., 61.4 grams of a second fraction was distilled over having a refractive index at 25° C. of 1.4308 which fraction was further identified as gamma-(N - 2 - carbomethoxyethyl) - aminopropyltriethoxysilane

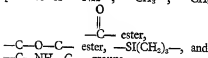


Analysis for C₁₂H₂₃NSiO₃:

Found: C, 51.0; H, 9.7; N, 4.4; Si, 9.3.

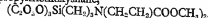
Calculated: C, 50.8; H, 9.5; N, 4.6; Si, 9.1.

The infrared spectrum confirmed the presence of -NH-, -CH₂-, -CH₂-,



Two higher boiling fractions were also obtained from the residue in the 250 cc. flask, namely, (1) 6.8 grams having a boiling range from 130° C. (at 0.33 mm. of Hg) to

145° C. (at 0.30 mm. of Hg), refractive index at 25° C. of 1.4382, and (2) 3.6 grams having a boiling range from 145° C. (at 0.30 mm. of Hg)-167° C. (at .90 mm. of Hg), refractive index at 25° C. of 1.4388. Fraction (2) above was further identified as gamma-(N - di - 2 - carbomethoxyethyl)aminopropyltriethoxysilane,



Analysis for C₁₇H₃₃NSiO₃:

Calculated: C, 51.9; H, 8.9; N, 3.1; Si, 7.1.

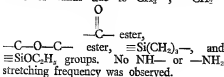
Found: C, 51.5; H, 8.4; N, 3.5; Si, 7.4.

EXAMPLE II

Reaction of Gamma-Aminopropyltriethoxysilane with Ethyl Acrylate

To the equipment described in Example I there were charged 100 grams of gamma-aminopropyltriethoxysilane and 100.1 grams of ethyl acrylate. The mixture was stirred for one hour during which time the tempera-

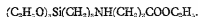
The infrared analysis confirmed the presence of bands due to CH₂-, -CH₂-



stretching frequency was observed.

ture 17° C. The reaction mixture was then heated to 120° C. for a period of 2 hours. Various fractions of the reaction product were distilled through a fractionating column under reduced pressure. A first fraction having a boiling range from 64° C. (at 1.2 mm. of Hg)—118° C. (at 1.4 mm. of Hg), $n_D^{25} = 1.4179$ —1.4360, amounted to 12 grams. At a temperature of 117° C.—121° C. and a

pressure of 0.45 mm. of Hg. 92.2 grams of a second fraction $n_D^{25} = 1.4302$, was collected which fraction was further identified as gamma - (N - 2 - carboethoxyethyl) - aminopropyltriethoxysilane,

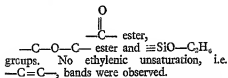


Analysis for $\text{C}_{14}\text{H}_{31}\text{O}_7\text{SiNO}_2$:

Calculated: C, 52.3; H, 9.7; Si, 8.7; N, 4.4.

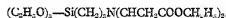
Found: C, 51.9; H, 9.0; Si, 9.2; N, 4.4.

Infrared analysis confirmed the presence of 20 bands due to —NH— ,



A third fraction amounting to 26.8 grams

was obtained having a boiling range from 149° C. (at 0.4 mm. of Hg)—166° C. (at 0.45 mm. of Hg) $n_D^{25} = 1.4372$ —1.4379. This fraction was further characterized as gamma - (N,N - di - 2 - carboethoxyethyl)aminopropyltriethoxysilane.



Analysis for $\text{C}_{18}\text{H}_{37}\text{SiNO}_7$:

Calculated: C, 54.2; H, 9.3; Si, 6.7; N, 3.3.

Found: C, 54.2; H, 9.0; Si, 7.1; N, 3.3.

The infrared spectrum did not disclose absorption due to —NH— , —NH_2 , or —C=C— bonding.

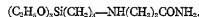
EXAMPLE III

Reaction of Gamma-Aminopropyltriethoxysilane with Acrylamide

To the equipment utilized in the previous examples (I and II), there were charged 110.7 grams of gamma-aminopropyltriethoxysilane and 39.1 grams of acrylamide added in 5 gram increments with continuous stirring of the reaction mixture. No temperature rise was observed. The mixture, i.e., slurry, was heated to 80° C. (at 56° C. the reaction mixture become homogeneous). The temperature of the resulting mixture was maintained at 80° C. for a period of 4 hours with continuous stirring. The reaction product was

distilled through a fractionating column under reduced pressure until a fraction amounting to 49.5 grams was collected. The fraction distilled at 85° C.—192° C. under a pressure of 1.52—2.5 mm. of Hg; refractive index at 25° C. was 1.4448—1.4521. An analytical sample had a boiling range from 85° C.—160° C. under a pressure from 1.5—2.3 mm. of Hg; the refractive index at 25° C. was 1.4448.

Infrared analysis of this analytical sample confirmed the presents of bands due to the presence of gamma - (N - 2 - amidoethyl)aminopropyltriethoxysilane,



Analysis for $\text{C}_{12}\text{H}_{26}\text{SiNO}_7$:

Calculated: C, 49.4; H, 9.6; Si, 9.6; N, 9.6.

Found: C, 49.3; H, 10.5; Si, 9.5; N, 9.6.

EXAMPLE IV

Reaction of Gamma-Aminopropyltriethoxysilane with Acrylonitrile

A 100 ml. flask was equipped with stirrer, dropping funnel, thermometer, and reflux condenser, and charged with 442.6 grams of gamma-aminopropyltriethoxysilane under a protective argon atmosphere and cooled to 5° C. with an ice bath. 213.4 grams of acrylonitrile was added dropwise, with continuous stirring, at a rate to maintain the temperature of the reagents below 30° C. After standing overnight, the reaction product was a water-white liquid weighing 655

grams having a refractive index at 25° C. of 1.4331. A portion of this material, i.e. 327.4 grams, was distilled through a fractionating column under reduced pressure. Three fractions were isolated possessing the following characteristics: (1) 30.4 grams; boiling range, 119° C.—132° C. at 0.7 mm. of Hg; $n_D^{25} = 1.4350$; (2) 210.6 grams; boiling range, 127° C.—132° C. at 0.6—0.7 mm. of Hg; $n_D^{25} = 1.4351$; (3) 10.5 grams; boiling range 122° C.—128° C. at 0.65 mm. of Hg; $n_D^{25} = 1.4351$. Fraction (2) above was further identified as gamma - (N - 2 - cyanoethyl)aminopropyltriethoxysilane,

(C₂H₅O)₂Si(CH₂)₆-NH(CH₂)₂CN
as follows:

Analysis for C₂₇H₅₈SiN₂O₂:

Calculated: N, 5.1 (by titration).

Found: N, 5.1 (by titration).

Infrared analysis confirmed the presence of bands due to -NH-, -CH₂-, -CH₂-, ≡SiC₂H₅, and -C≡N (non-conjugated) groups.

EXAMPLE V

Reaction of Delta-Aminobutyltriethoxysilane with Acrylonitrile

Employing the equipment set forth in Example I there was charged 282.2 grams of delta-aminobutyltriethoxysilane and 66.3 grams of acrylonitrile; the resulting mixture was continuously stirred at room temperature

for 1 hour. The infrared spectrum of the reaction product disclosed absorption due to -NH-, -C≡N, and ≡SiOC₂H₅ groups. No -C=C band was observed. The reaction product was subsequently distilled through a fractionating under reduced pressure wherein three fractions were obtained. The first fraction amounted to 74.6 grams having a boiling range from 56° C.-127° C. at a pressure of 0.4-0.5 mm. of Hg; the refractive index at 25°C. was 1.4238-1.4352. A second fraction amounted to 212.1 grams with a boiling range of 128° C.-135° C. at a pressure of 0.3-0.4 mm. of Hg; n_D²⁵ = 1.4370. This fraction was shown to be delta-(N-2-cyanoethyl)aminobutyltriethoxysilane. (C₂H₅O)₂Si(CH₂)₆-NH(CH₂)₂CN.

Microanalysis for C₁₄H₂₈SiN₂O₂:

Calculated: C, 54.1; H, 9.8; Si, 9.8; N, 9.7.

Found: C, 52.5; H, 10.4; Si, 10.0; N, 9.7.

The infrared analysis showed this material to possess -NH- bands; no -NH₂ bands were observed.

19.6 grams of a third fraction was isolated having a boiling range of 172° C.-210° C. at 0.52-0.98 mm. of Hg; the refractive index

at 25° C. was 1.4484. This material was further shown to be delta-(N,N-di-2-cyanoethyl)aminobutyltriethoxysilane, (C₂H₅O)₂Si(CH₂)₆N(CH₂CH₂CN)₂.

Analysis for C₁₆H₃₂SiN₄O₂:

Calculated: C, 56.4; H, 9.1; Si, 8.2; N, 12.2.

Found: C, 54.9; H, 9.4; Si, 9.4; N, 11.7.

The infrared spectrum showed strong -C=N bands and no -NH- bands.

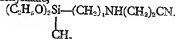
EXAMPLE VI

Reaction of Delta-Aminobutylmethyldiethoxysilane with Acrylonitrile.

A 100 ml. flask equipped as described in Example IV was charged with 205.3 grams of delta-aminobutylmethyldiethoxysilane. 105.2 grams of acrylonitrile was added dropwise with constant stirring of the solution. During the dropwise addition the temperature rose from 25° C. to 48° C., and at the latter temperature the solution was stirred for an additional 2 hours. Upon allowing the solution to stand for 2 days at room temperature, the resulting reaction product was distilled through a fractionating column

under reduced pressure. Three fractions were obtained, namely, (1) 50.7 grams with a boiling range of 64° C.-115° C. at a pressure of 0.50 mm. of Hg; n_D²⁵ = 1.4209-1.4210; (2) 165.9 grams with a boiling point of 115° C.-116° C. at 0.90 mm. of Hg pressure; n_D²⁵ = 1.4423; and (3) 9.7 grams with a boiling point of 183° C.-184° C. at 0.89 mm. of Hg pressure; n_D²⁵ = 1.4518.

Fraction (2) above was further identified as delta-(N-2-cyanoethyl)butylmethyldiethoxysilane,



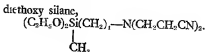
Microanalysis for C₁₂H₂₄SiN₂O₂:

Calculated: C, 55.8; H, 10.1; N, 10.8; Si, 10.9.

Found: C, 54.1; H, 10.8; N, 10.9; Si, 10.7.

The infrared spectrum confirmed the presence of -NH-, -C≡N, ≡SiCH₃, and ≡SiOC₂H₅ groups. No evidence of -C=C bands were present.

Fraction (3) above was shown to be delta-(N,N-di-2-cyanoethyl)aminobutylmethyldiethoxysilane,



Analysis for C₁₈H₃₂SiN₄O₂:

Calculated: C, 57.8; H, 9.4; N, 13.5; Si, 9.0.

Found: C, 56.1; H, 10.9; N, 12.2; Si, 10.2.

EXAMPLE VII

Reaction of Delta-Aminobutylmethyldiethoxysilane with Ethyl Cinnamate

To the equipment described in Example I there were charged 102.7 grams of delta-aminobutylmethyldiethoxysilane and 88.1 grams of ethyl cinnamate. The resulting mixture was stirred for 1 hour at room temperature and allowed to stand overnight. On

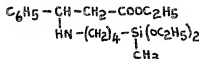
Calculated: C, 63.0; H, 10.4; Si, 6.24; N, 3.7.

heating this mixture to 180° C. an orange color developed. Employing a fractionating column under reduced pressure a 10.7 grams fraction of delta - (N - 1 - phenyl - 2 - carbethoxyethyl)aminobutylmethyldiethoxysilane, having a boiling range of 152° C.-162° C. at 0.5 mm. of Hg. and refractive index at 25° C. of 1.4776 was obtained.

Analysis for C₂₀H₂₇SiNO₃:

Calculated: C, 63.0; H, 10.4; Si, 6.24; N, 3.7.

The structure of the product was further confirmed by infrared analysis and identified as:



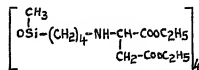
EXAMPLE VIII

Reaction of Delta-Aminobutylmethyldiethoxysilane with Diethyl Malate

To the equipment set forth in Example I there was charged 102.7 grams of delta-aminobutylmethyldiethoxysilane and 86.1 grams of diethyl malate. The temperature of the reaction mixture rose to

Calculated: C, 51.5; H, 10.3; Si, 48.3; N, 6.3.

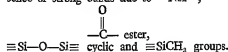
85° C. The reaction product could not be distilled, but was stripped under 1.0 mm. pressure up to 150° C. until 20.0 grams of distillate was collected in the cold trap. The residue, a viscous oil, was identified as the cyclic tetramer of delta - (N - 1,2 - dicarboethoxyethyl)aminobutylmethyldiethoxysilane unit.



Analysis for the delta - (N - 1,2 - dicarboethoxyethyl)aminobutylmethyldiethoxysilane unit.

Calculated: C, 51.5; H, 10.3; Si, 48.3; N, 6.3.

The infrared spectrum confirmed the presence of strong bands due to —NH—,



EXAMPLE IX

Reaction of Dimethylsilicone Oil (1,000 M.W.) Modified with 10 Weight Per Cent Delta-Aminobutylmethyldiethoxysilane Units with Methyl Acrylate

To a 500 cc. flask there were charged 100 grams of a trimethylsiloxy end-blocked dimethylsiloxane oil (M.W. 1,000) containing 10 weight per cent delta-aminobutylmethyldiethoxysilane units and 6.55 grams of methyl acrylate. The mixture was allowed to stand overnight.

The resulting oil, a tri-methylsiloxy end-blocked dimethylsiloxane oil containing delta-(N - 2 - carbomethoxyethyl)aminobutylmethyldiethoxysilane units had a refractive index at 25° C. of 1.4090. The infrared spectrum confirmed the presence of —NH—, linear ≡SiOSi≡, =Si(CH₃)₂ and —Si(CH₃)₃ groups.

EXAMPLE X

Reaction of a Dimethylsilicone Oil (M.W. 1,000) Containing 10 weight Per Cent Delta - Aminobutylmethyldiethoxysilane Units with Ethyl Acrylate

Utilizing the equipment described in Example I there were charged 200 grams of a 1,000 M.W. trimethylsiloxy end-blocked dimethylsiloxane oil containing 10 weight per cent delta-aminobutylmethyldiethoxysilane units and 22.2 grams of ethyl acrylate. The mixture was stirred for 1 hour at a maximum temperature of 110° C. The product oil was then sparged under reduced pressure to a pot temperature of 100° C. The product, a trimethylsiloxy end-blocked dimethylsiloxane oil containing gamma - (N - 2 - carbomethoxyethyl)aminobutylmethyldiethoxysilane units, had a viscosity of 40 centipoises and a refractive index at 25° C. of 1.4122.

Microanalysis: Per cent nitrogen determined by titration:

Calculated: N, 1.27.
Found: N, 1.29.

The infrared analysis confirmed the presence of linear —SiO—Si— ,



and —NH— groups. The oil was soluble in ethanol and benzene and insoluble in water.

EXAMPLE XI

Reduction of $(\text{C}_6\text{H}_5\text{O})_2\text{Si}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{CN}$ to Prepare $(\text{C}_6\text{H}_5\text{O})_2\text{Si}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$

To a 300 cc. steel rocking autoclave there was charged 145 grams of $(\text{C}_6\text{H}_5\text{O})_2\text{Si}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{CN}$ (prepared in Example V), followed by flushing the autoclave with argon. 8 grams of Raney nickel was then added and ammonia was introduced until the pressure was 100 psi. The introduction of hydrogen at 25° C. raised the pressure of the autoclave to 1500 psi, and the vessel was heated to 120° C. for a period of 5 hours. The reaction was carried out over a period of 17 hours. The

total pressure drop of hydrogen was 2120 psi. The vessel was then cooled to 25° C.; the pressure was 700 psi, and the contents were examined. Since reduction was incomplete (determined by titration of the product with standard HCl), the liquid reaction product was filtered, 8.0 grams of bis-(cyclopentadienyl) nickel was added and the above reduction step was repeated, i.e., ammonia (100 psi) and hydrogen (total pressure of 1500 psi) were added as above and the vessel was heated at 132° C. for 2 hours and at 142° C. for 18 hours. A brown liquid product was obtained and filtered. An attempt to distill this product at reduced pressure disclosed evidence of dissociation, consequently, the product was stripped under a pressure of 1.0 mm. of Hg and employing a pot temperature up to 165° C. The stripped brown liquid product was delta-(N - 3 - aminopropyl)aminobutyltriethoxysilane, $(\text{C}_6\text{H}_5\text{O})_2\text{Si}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$.

Analysis for $\text{C}_{23}\text{H}_{32}\text{SiN}_2\text{O}_2$:

Calculated: C, 53.4; H, 11.0; Si, 9.6; N, 9.6.

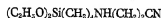
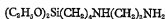
Found: C, 53.2; H, 11.1; Si, 10.4; N, 9.5 (titrated).

EXAMPLE XII

Reduction of



to Yield



was reduced in a manner similar to that described in Example XI using a 75.0 gram charge. 75 cc. of ethanol was employed as a solvent, and ammonia added until the autoclave pressure was 250 psi at 250° C. 8.0 grams of Raney nickel was used as the catalyst. The reduction was carried out at a temperature of 130° C.—132° C. for a period of 15 hours. The product was removed from the autoclave and stripped under a reduced pressure of 1.0 mm. of Hg and a maximum pot temperature of 100° C. The residue delta-(N,N - di - 3 - aminopropyl)aminobutylmethyldiethoxysilane weighed 55.5 grams.

Analysis for $\text{C}_{23}\text{H}_{34}\text{SiN}_2\text{O}_2$:

Calculated: C, 54.9; H, 11.5; Si, 10.7; N, 10.7.

Found: C, 53.2; H, 12.9; Si, 12.2; N, 10.0.

The infrared spectrum confirmed the presence of —NH_2 , $\equiv\text{SiCH}_3$, and $\equiv\text{SiOC}_6\text{H}_5$ groups. No $\text{—C}\equiv\text{N}$ bands were observed.

EXAMPLE XIII

Hydrolysis of $(\text{C}_6\text{H}_5\text{O})_2\text{Si}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{COOCH}_3$ to Yield $\text{O}_2\text{Si}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{COOCH}_3$

To a 100 ml. flask there was charged 32.0 grams of

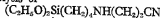


This material was cooled in an ice bath and a mixture of 18 grams of water and 15 ml. of concentrated hydrochloric acid was added with stirring being effected by a stream of

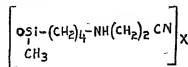
argon gas passing through the resulting solution. The temperature was not permitted to exceed 33° C. Water and alcohol were stripped from the liquid product by employing a pot temperature up to 100° C. (hot water bath) at a pressure of 1—5 mm. of Hg for a period of 2 hours. The white resin product, gamma-(N - 2 - carbomethoxyethyl)-aminopropylpolysiloxane, weighed 24.7 grams.

EXAMPLE XIV

Hydrolysis of



To prepare



To a 200 cc. flask there was charged 75.0 grams of

- 5 $(\text{C}_6\text{H}_5)_3\text{Si}-(\text{CH}_2)_4\text{NH}(\text{CH}_2)_2\text{CN}$.
- 36 ml. of water was then added with swirling of the contents in the flask. The resulting mixture was not homogeneous, and no heat effect was noted on mixing. The mixture
- 10 was heated to reflux temperature for 1 hour during which period the contents became a homogeneous, colorless liquid. The liquid product was stripped up to a pot temperature of 205° C. under an argon atmosphere, yielding
- 15 a pale yellow homogeneous oil residue. The residue was further stripped at a pot temperature up to 149° C. for a period of 25 minutes yielding 53.5 grams of delta-(N-2-cyanoethyl)aminoethylmethylpolysiloxane, a pale yellow liquid possessing the following characteristics: $n_D^{25}=1.4772$; vis-
- 20

cosity of 1810 centipoises at 25° C., M.W.=2300.

Microanalysis for $\text{C}_6\text{H}_{13}\text{SiH}_5\text{O}$:

Calculated: Si, 15.2; N, 7.6 (titration). 25
Found: Si, 15.1; N, 7.4

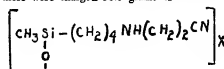
The infrared analysis of this material confirmed the presence of $-\text{NH}-$, $-\text{C}\equiv\text{N}$, $\equiv\text{SiCH}_3$, $\equiv\text{SiOSi}\equiv$, and $\equiv\text{Si}(\text{CH}_3)_2-$ groups. 30

EXAMPLE XV

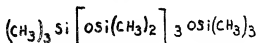
Preparation of a Dimethylsilicone Oil (M.W.=5,000) Containing 10 Weight Per Cent $-\text{OSi}-(\text{CH}_2)_4\text{NH}(\text{CH}_2)_2\text{CN}$ Units



To the equipment described in Example I 35 there were charged 30.0 grams of



(prepared in Example XIV), 247.0 grams of dimethylsiloxane cyclic tetramer, and 23.0 grams of 40



- This mixture was heated to 158° C., with stirring, and 30 drops of potassium silanolate (containing 70 p.p.m. of K) catalyst were
- 45 added. The homogeneous solution was allowed to stand overnight at 158° C. The contents were then cooled to below 100° C. and 6 drops of acetic acid were added, followed by stirring for 10 minutes and sparging under an argon atmosphere at a temperature in the range of 120° C.—140° C.,
- 50 a pressure of 5.0 mm. of Hg, and a period of time of 2 hours. The product, a trimethylsiloxy end-blocked dimethylpolysiloxane oil containing delta-(N-2-cyanoethyl)aminoethylmethylsiloxane units, a light yellow oil, weighed 275 grams, possessed a viscosity of 103.7 cs., and a viscosity temperature index of 0.653.
- 55

- 60 Microanalysis for Percent

Calculated: N, 0.83

Found: N, 0.94 (titration)

EXAMPLE XVI

- Reaction of
- 65 $(\text{C}_6\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_4\text{NH}(\text{CH}_2)_2\text{COOC}_2\text{H}_5$ with Silica Gel to Form a Silicone Chelating Resin
- Silica gel, 150 cc., of 6 mesh size was slurried in 350 cc. of water until it crumbled

to about 60 mesh size, followed by drying 70 at 110° C. for 1 hour. The silica gel (60 mesh) was then placed in a 500 cc. flask equipped with condenser and stirrer, and 160 cc. of toluene containing 10 grams of

$(\text{C}_6\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_4\text{NH}(\text{CH}_2)_2\text{COOC}_2\text{H}_5$ 75 was added thereto. The mixture was stirred and heated to a temperature from about 90° C.—100° C. for 15 minutes. The product was then cooled, filtered, washed with petroleum ether, and heated in an air oven at 110° C. for 1 hour. Titration with standard HCl showed that 85% of the silane had been absorbed by the silica gel. 98 grams of the treated silica gel was then charged to a vessel containing 125 cc. of water and 0.1—0.2 gram of potassium hydroxide and stirred at 90° C. for 1 hour. The contents were allowed to stand overnight at room temperature. The treated silica gel was recovered by washing with water and acetone and briefly dried by air. 60 grams of this material was placed in a vertical glass column, 1" diameter x 24" length, and water was added thereto. 5 cc. of 0.1 N aqueous cupric acetate was passed slowly into the column followed by a large amount of water. The copper was adsorbed and formed a blue zone on the silica gel-silicone packing. Continued washings with water did not improve the 95

- copper. Adsorption was quantitative since the ammonia test did not detect any copper in the elutriant. The blue color was most intense near the top of the column. Concentrated acetic acid was then passed through the column quantitatively removing copper from the silica gel-silicone packing to give a blue elutriant. The column was then washed with water until the elutriant was barely acidic as determined by litmus paper. Aqueous cupric acetate was again added to the column in the same quantity as above and the procedure was repeated. Copper adsorption on the silica gel was again quantitative.
- As a control, a column packed solely with a silica gel was treated with aqueous cupric acetate under the same conditions as described above for the silicone-treated silica gel. The copper was not adsorbed.
- 5 cc. of 0.1 N aqueous nickel acetate was passed into a column containing silicone-treated silica gel under conditions similar to those used for the adsorption of copper above. Adsorption of nickel was quantitative, and repeated washings with water did not disclose the presence of nickel in the elutriant.

EXAMPLE XVII

Flocculation of Clay by

- $\text{NH}_2(\text{CH}_2)_6\text{NH}(\text{CH}_2)_6\text{Si}(\text{OC}_2\text{H}_5)_3$ and $\text{C}_6\text{H}_5\text{OOC}(\text{CH}_2)_6\text{NH}(\text{CH}_2)_6\text{Si}(\text{OC}_2\text{H}_5)_3$ The compounds $\text{NH}_2(\text{CH}_2)_6\text{NH}(\text{CH}_2)_6\text{Si}(\text{OC}_2\text{H}_5)_3$ (I) and $\text{C}_6\text{H}_5\text{OOC}(\text{CH}_2)_6\text{NH}(\text{CH}_2)_6\text{Si}(\text{OC}_2\text{H}_5)_3$ (II) were tested as flocculating, or depeptizing, agents for clay in the following manner: To a test tube there were added 10 cc. of water, 0.3 gram of a brown clay, and compound (I) above. The test tube was vigorously shaken and the clay allowed to settle. The procedure was repeated for compound (II) above. A control sample, i.e., no added silicone compound, was run simultaneously. Effectiveness of the additive was judged by both the degree of flocculation and the rapidity of settling of the clay particles. The tests showed that compound (I) effectively flocculated the clay particles and increased the rate of settling of the particles over that of the control sample. Compound (II) was not as outstanding as compound (I), but compound (II) disclosed suitable flocculating properties.

WHAT WE CLAIM IS:—

1. Process for the production of organo-silicon compounds containing a substituted amino group attached to a silicon atom through a polymethylene linkage of at least three carbon atoms, characterized by reacting an aminoalkyl silicon compound containing the reactive group:



wherein a is an integer of at least 3, with

an alpha-beta olefinically unsaturated organic compound represented by the formula:



wherein B is a hydrogen atom, or an alkyl or aryl radical or the radical represented by X; R^{II} is hydrogen or an alkyl radical; and X is a nitrile radical or a substituted carbonyl radical as represented by the formula:



wherein D is a hydrogen atom or an alkyl, aryl, alkoxy, aryloxy or amino radical and when the olefinically unsaturated organic compound is an aliphatic nitrile, if desired, hydrolyzing the resulting cyanoalkylaminoalkyl silicon compound to yield an aminoalkyl-aminoalkyl silicon compound.

2. The process as claimed in claim 1, wherein the aminoalkylsilicon compound is an aminoalkyl silane represented by the formula:



in which R is an alkyl or aryl radical; Y is an alkoxy radical; a is an integer of at least 3; and b is 0, 1 or 2.

3. The process as claimed in claim 1, wherein the aminoalkylsilicon compound is an aminoalkylpolysiloxane.

4. The process as claimed in claim 2, in which the amino-substituted silane produced is hydrolysed and condensed to form a corresponding polysiloxane.

5. The process as claimed in claims 1, 2 or 3, wherein the alpha-beta olefinically unsaturated compound is methyl acrylate, acrylamide, acrylonitrile, ethyl cinnamate, or diethyl maleate.

6. The process as claimed in claim 2, wherein the aminoalkyl silicon compound is gamma-aminopropyltriethoxysilane, the alpha-beta olefinically unsaturated compound is methyl acrylate, and the organosilicon compound produced is gamma - (N - 2 - carbomethoxyethoxyethyl) - aminopropyltriethoxysilane.

7. The process as claimed in claim 2, wherein the aminoalkyl silicon compound is gamma-aminopropyltriethoxysilane, the alpha-beta olefinically unsaturated compound is acrylamide, and the organosilicon compound produced is gamma - (N - 2 - amidoethyl)-aminopropyltriethoxysilane.

8. The process as claimed in claim 2, wherein the aminoalkyl silicon compound is gamma-aminopropyltriethoxysilane, the alpha-beta olefinically unsaturated compound is methyl acrylate, and the organosilicon compound produced is gamma - (N,N - di - 2 - carbomethoxyethyl) - aminopropyltriethoxysilane.

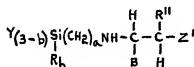
9. The process as claimed in claim 2, wherein the aminoalkyl silicon compound is gamma-aminopropyltriethoxysilane, the alpha-beta olefinically unsaturated compound is acrylonitrile, and the organosilicon compound produced is gamma - (N - 2 - cyanoethyl)-aminopropyltriethoxysilane.

10. The process as claimed in claim 3 wherein the aminoalkyl silicon compound is delta - aminobutylmethylsiloxane cyclic tetramer, the alpha-beta olefinically unsaturated compound is diethyl maleate, and the organosilicon compound produced is the cyclic tetramer of delta - (N - 1,2 - dicarbomethoxyethyl) - aminobutylmethylsiloxane.

11. The process as claimed in claim 3, wherein the aminoalkylsilicon compound is dimethylsiloxane oil modified with delta-aminobutylmethylsiloxo units, the alpha-beta olefinically unsaturated compound is ethyl acrylate, and the organosilicon compound produced is a dimethylsiloxane containing delta - (N - 2 - carbomethoxyethyl) - aminobutylmethylsiloxane units.

12. The process claimed in claim 1 substantially as herein described in any one of Examples I to XVI.

13. An organosilicon compound represented by the formula:

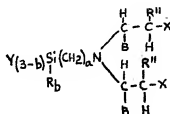


wherein R is an alkyl or aryl radical; Y is an alkoxy radical; Z' is an aminoalkyl radical or the radical represented by X; B is hydrogen or an alkyl, or aryl radical, or the radical represented by X; X is a nitrile radical, or a substituted carbonyl radical as represented by the formula:



wherein D is hydrogen or an alkyl, aryl, alkoxy, aryloxy, or amino radical; R'' is hydrogen or an alkyl radical; a is an integer of at least 3; and b is 0, 1 or 2.

14. An organosilicon silane represented by the structural formula:

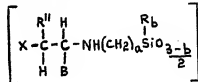


wherein R is an alkyl or aryl radical; Y is an alkoxy radical; B is hydrogen or an alkyl or aryl radical, or the radical represented by X group; X is a nitrile radical or a substituted carbonyl radical represented by the formula:



wherein D is hydrogen or an alkyl, aryl, alkoxy, aryloxy, or amino radical; R'' is hydrogen or alkyl radical; a is an integer of at least 3; and b is 0, 1 or 2.

15. A siloxane polymer or siloxane copolymer containing units represented by the structural formula:

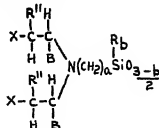


wherein R is an alkyl or aryl radical; B is hydrogen or an alkyl or aryl radical, or the radical represented by X; X is a nitrile radical or a substituted carbonyl radical as represented by the formula:



wherein D is hydrogen or an alkyl, aryl, alkoxy, aryloxy, or amino radical; R'' is hydrogen or an alkyl radical; a is an integer of at least 3; and b is 0, 1 or 2.

16. A siloxane polymer or siloxane copolymer containing units represented by the structural formula:



wherein R is an alkyl or aryl radical; B is hydrogen or an alkyl or aryl radical, or the radical represented by X; X is a nitrile radical or a substituted carbonyl radical as represented by the formula:



wherein D is hydrogen or an alkyl, aryl, alkoxyl, aryloxy, or amino radical; R¹ is hydrogen or an alkyl radical; a is an integer of at least 3; and b is 0, 1 or 2.

17. Gamma - (N - 2 - carbomethoxyethyl) - aminopropyltriethoxysilane.

18. Gamma - (N,N - di - 2 - carbomethoxyethyl) - aminopropyltriethoxysilane.

19. Gamma - (N - 2 - carbethoxyethyl) - aminopropyltriethoxysilane.

20. Gamma - (N,N - di - 2 - carbethoxyethyl) - aminopropyltriethoxysilane.

21. Gamma - (N - 2 - amidoethyl) - aminopropyltriethoxysilane.

22. Gamma - (N - 2 - cyanoethyl) - aminopropyltriethoxysilane.

23. Delta - (N - 2 - cyanoethyl) - aminobutyltriethoxysilane.

24. Delta - (N,N - di - 2 - cyanoethyl) - aminobutyltriethoxysilane.

25. Delta - (N - 2 - cyanoethyl) - butylmethyldiethoxysilane.

26. Delta - (N,N - di - 2 - cyanoethyl) - aminobutylmethyldiethoxysilane.

27. Delta - (N - 1 - phenyl - 2 - carbethoxyethyl) - aminobutylmethyldiethoxysilane.

28. The cyclic tetramer of delta - (N - 1,2 - dicarbethoxyethyl) - aminobutylmethyloxane.

29. A trimethylsiloxy end - blocked dimethylsiloxane oil containing delta - (N - 2 - carbomethoxyethyl) - aminobutylmethyloxane units.

30. A trimethylsiloxy end - blocked dimethylsiloxane oil containing delta - (N - 2 - carbomethoxyethyl) - aminobutylmethyloxane units.

31. Delta - (N - 3 - aminopropyl) - aminobutyltriethoxysilane.

32. Delta - (N,N - di - 3 - aminopropyl) - aminobutylmethyldiethoxysilane.

33. Gamma - (N - 2 - carbomethoxyethyl) - aminopropylpolysiloxane.

34. Delta - (N - 2 - cyanoethyl) - aminobutylmethyldiethoxysilane.

35. A trimethylsiloxy end-blocked dimethylsiloxane oil containing delta - (N - 2 - cyanoethyl) - aminobutylmethyloxane units.

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Chartered Patent Agents.

Reference has been directed in pursuance of Section 9, subsection (1) of the Patents Act, 1949, to Patents Nos. 795,894, 769,498 and 684,296.

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